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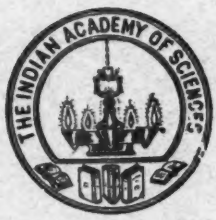

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EINIGE DIOPHANTISCHE PROBLEME UND ZAHLENTHEORETISCHE RESULTATE.

By Alfred Moessner,
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Received July 24, 1937.
(Communicated by Sir C. V. Raman, Kt., F.R.S., N.L.)

I (α) Gilt die Relation $A_1, A_2, A_3, \cdots, A_z \overset{n}{=} B_1, B_2, B_3, \cdots, B_z$ für $n = 1, 2$, dann gilt für beliebiges h auch die Relation

$A_1, A_2, A_3, \cdots, A_z, B_1 + h, B_2 + h, B_3 + h, \cdots, B_z + h \overset{n}{=} B_1, B_2, B_3, \cdots, B_z, A_1 + h, A_2 + h, A_3 + h, \cdots, A_z + h$ für $n = 1, 2, 3$.

Anmerkung: Das Symbol $\overset{n}{=}$ bedeutet gleiche Potenzsummen für n Exponenten. So bedeutet $a, b, c, d \overset{n}{=} e, f, g, j$ für $n = 1, 2, 3$ das System

$$\begin{cases} a + b + c + d = e + f + g + j \\ a^2 + b^2 + c^2 + d^2 = e^2 + f^2 + g^2 + j^2 \\ a^3 + b^3 + c^3 + d^3 = e^3 + f^3 + g^3 + j^3. \end{cases}$$

Gilt die Relation $A_1, A_2, A_3, \cdots, A_z \overset{n}{=} B_1, B_2, B_3, \cdots, B_z$ für $n = 1, 2, \cdots, k$, dann gilt generell

$A_1, A_2, A_3, \cdots, A_z, B_1 + h, B_2 + h, B_3 + h, \cdots, B_z + h \overset{n}{=} B_1, B_2, B_3, \cdots, B_z, A_1 + h, A_2 + h, A_3 + h, \cdots, A_z + h$ für $n = 1, 2, \cdots, k, k + 1$.

Gilt $A_1, A_2, \cdots, A_z = B_1, B_2, \cdots, B_z$, dann gilt auch für beliebiges h die Relation

$A_1, A_2, \cdots, A_z, B_1 + h, B_2 + h, \cdots, B_z + h \overset{n}{=} B_1, B_2, \cdots, B_z, A_1 + h, A_2 + h, \cdots, A_z + h$ für $n = 1, 2$.

(β) Besteht die Identität $C^v + D^v = E^v = O^v + E^v$, so folgt, wenn $h = E^v$ ist, die Identität

$C^v, D^v, 2E^v \overset{n}{=} (C^v + E^v), (D^v + E^v)$ für $n = 1, 2$.

Diese Identität ist für $v > 2$ mit ganzen rationalen Zahlen unmöglich, wenn das große Fermatsche Theorem richtig ist.

(γ) Ist $a^2 + b^2 = 0^2 + c^2$, dann gilt für beliebiges t die Relation $(t - b), (t - a), (t + a), (t + b) \overset{n}{=} (t - c), (t + c)\ t, t$ für $n = 1, 2, 3$.

So ergibt die Relation $(\sqrt{2})^2 + (\sqrt{2})^2 = 0^2 + 2^2$ für $t = 5$ das Kuriosum $(5 - \sqrt{2}), (5 - \sqrt{2}), (5 + \sqrt{2}), (5 + \sqrt{2}) \overset{n}{=} (5 - 2), (5 + 2)\ 5, 5$ für $n = 1, 2, 3$.

(δ) Gilt die Relation $A_1, A_2, A_3, \cdots, A_z \overset{n}{=} B_1, B_2, B_3, \cdots, B_z$ für $n = 1, 2, \cdots, k$, dann gilt für beliebiges x auch die Relation

$$(A_1 + x)^{k+1} + (A_2 + x)^{k+1} + (A_3 + x)^{k+1} + \cdots + (A_z + x)^{k+1} - (B_1 + x)^{k+1} - (B_2 + x)^{k+1} - (B_3 + x)^{k+1} - \cdots - (B_z + x)^{k+1} = F,$$

wenn $z = k + 1$ ist.

Zwei Sonderfälle:

$$(1 + x)^6 + (4 + x)^6 + (6 + x)^6 + (12 + x)^6 + (14 + x)^6 + (17 + x)^6 - 2\,[(2 + x)^6 + (9 + x)^6 + (16 + x)^6] = 86400.$$

$$(5^2 + x)^3 + (6^2 + x)^3 + (11^2 + x)^3 - (1^2 + x)^3 - (9^2 + x)^3 - (10^2 + x)^3 = 302400.$$

x ist in beiden Fällen beliebig.

Bei der angegebenen Kondition gilt auch die Identität

$$(A_1 + y) \cdot (A_2 + y) \cdot (A_3 + y) \cdots (A_z + y) - (B_1 + y) \cdot (B_2 + y) \cdot (B_3 + y) \cdots (B_z + y) = G$$ für beliebiges y wobei G konstant bleibt.

Es sei $k = v_1 \cdot v_2 \cdot v_3 \cdot v_4 \cdots \cdot v_r$. Dann ergibt die Anwendung der Theoreme unter (α) also r verschiedene Identitäten von der Form

$A_1^v, A_2^v, \cdots, A_z^v, (B_1^v + h), (B_2^v + h), \cdots, (B_z^v + h) \overset{n}{=} B_1^v, B_2^v, \cdots, B_z^v, (A_1^v + h), (A_2^v + h), \cdots, (A_z^v + h)$ für $n = 1, 2, \cdots, p$ bei beliebigem z und h.

Exempel: 1, 5, 10, 16, 27, 28, 38, 39 $\overset{n}{=}$ 2, 3, 13, 14, 25, 31, 36, 40 für $n = 1, 2, 3, 4, 5, 6$ (*cf.* A. Moessner, "Die Gleichung $A_1^n + A_2^n + \cdots + A_z^n = B_1^n + B_2^n + \cdots + B_z^n$, $n = 1, 2, \cdots, 8$ und verwandte Formen" in *The Tohoku Math. Journal*, Vol. 41, Part I) ergibt, da $6 = 1 \cdot 6 = 2 \cdot 3$, folgende Identitäten für $h = 1$:

(1) $1, 5, 10, \cdots, 39, (2 + 1), (3 + 1), (13 + 1), \cdots, (40 + 1) \overset{n}{=} 2, 3, 13, \cdots, 40, (1 + 1), (5 + 1), (10 + 1), \cdots, (39 + 1)$ für $n = 1, 2, \cdots, 7$; $v = 1$.

(2) $1^2, 5^2, 10^2, \cdots, 39^2, (2^2 + 1), (3^2 + 1), \cdots, (40^2 + 1) \overset{n}{=} 2^2, 3^2, \cdots, 40^2, (1^2 + 1), (5^2 + 1), \cdots, (39^2 + 1)$ für $n = 1, 2, 3, 4$; $v = 2$.

(3) $1^3, 5^3, \cdots, 39^3, (2^3 + 1), (3^3 + 1), \cdots, (40^3 + 1) \overset{n}{=} 2^3, 3^3, \cdots, 40^3, (1^3 + 1), (5^3 + 1), \cdots, (39^3 + 1)$ für $n = 1, 2, 3$; $v = 3$.

(4) $1^6, 5^6, \cdots, 39^6, (2^6 + 1), (3^6 + 1), \cdots, (40^6 + 1) \overset{n}{=} 2^6, 3^6, \cdots, 40^6, (1^6 + 1), (5^6 + 1), \cdots, (39^6 + 1)$ für $n = 1, 2$; $v = 6$.

II. Man bekommt Lösungen der Relation $H_1, H_2, H_3 \overset{n}{=} K_1, K_2, K_3$ für $n = 1, 3$, wenn man setzt

$$H_1 = m^2p - mp^2 - qr^2 - q^2r + 2\,pqr;$$

$$H_2 = m^2p + mp^2 + q^2r + qr^2 - 2\,mqr - 2\,pqr;$$

$$H_3 = -m^2p + mp^2 - q^2r - qr^2 + 2mqr;$$
$$K_1 = m^2p + mp^2 - q^2r + qr^2 - 2mpr;$$
$$K_2 = -m^2p - mp^2 - q^2r - qr^2 + 2mpq + 2mpr;$$
$$K_3 = m^2p + mp^2 + q^2r - qr^2 - 2mpq.$$

Wählt man nun m, p, q, r so, daß $H_1, H_2, H_3, K_1, K_2, K_3$ rationale ganzzahlige Quadrate ergeben, so bekommt man Lösungen der Equation

$\begin{cases} M^2 + N^2 + P^2 = Q^2 + R^2 + S^2 \\ M^6 + N^6 + P^6 = Q^6 + R^6 + S^6 \end{cases}$ in ganzen rationalen Numbers. Setzt man $m = \frac{37}{26}$, $p = \frac{13}{4}$, $q = \frac{5}{4}$, $r = \frac{29}{16}$, so bekommt man, wenn man zuletzt noch durch den gemeinsamen Faktor 16 kürzt, die Lösung

$\begin{cases} 3^2 + 19^2 + 22^2 = 10^2 + 15^2 + 23^2 \\ 3^6 + 19^6 + 22^6 = 10^6 + 15^6 + 23^6. \end{cases}$ Für die linke Seite dieses Resultats gilt zugleich: $\begin{cases} 3^2 + 19^2 + (3+19)^2 = 6^2 + 17^2 + (6+17)^2 \\ 3^4 + 19^4 + (3+19)^4 = 6^4 + 17^4 + (6+17)^4. \end{cases}$

(ϵ) Es ist $\frac{x}{x-1} \cdot x = \frac{x}{x-1} + x;$

$$\frac{x}{\sqrt{x}-1} : \sqrt{x} = \frac{x}{\sqrt{x}-1} - \sqrt{x};$$

Ist $t = \sqrt{\left(\frac{y}{2}\right)^2 - y}$, dann gilt $y = \left(\frac{y}{2} + t\right) \cdot \frac{y}{\frac{y}{2} + t} =$

$$\left(\frac{y}{2} + t\right) + \frac{y}{\frac{y}{2} + t}.$$

Wir bekommen durch diese Formeln Solutionen der Relationen $V \cdot U = V + U$; $P : T = P - T$.

Ich gebe ein paar Exempel:

$$2 = 1 + \sqrt{-1} \cdot \frac{2}{1+\sqrt{-1}} = 1 + \sqrt{-1} + \frac{2}{1+\sqrt{-1}};$$

$$4 = 2 \cdot 2 = 2 + 2;$$

$6 = 3 + \sqrt{3} \cdot \frac{6}{3+\sqrt{3}} = 3 + \sqrt{3} + \frac{6}{3+\sqrt{3}}$; Bemerkung: Es ist aber auch $6 = 1 \cdot 2 \cdot 3 = 1 + 2 + 3$.

$$7\tfrac{1}{5} = (1\tfrac{8}{5} + 5\tfrac{1}{25}) \cdot \frac{7\frac{1}{5}}{1\frac{8}{5} + 5\frac{1}{25}} = (1\tfrac{8}{5} + 5\tfrac{1}{25}) + \frac{7\frac{1}{5}}{1\frac{8}{5} + 5\frac{1}{25}} = 1\tfrac{1}{5} \cdot 6 = 1\tfrac{1}{5} + 6.$$

III. *Theorem*: Die Relation $x^2 - y^2 = y^2 - z^2 = v^2$ hat keine Solution in ganzen rationalen Numbers, wenn $v \neq 0$ ist.

Proof: Wir lösen zuerst das System

$$x^2 - y^2 = y^2 - z^2 > 0 \qquad (x > 0, y > 0, z > 0).$$

Dabei kann man x, y, z zu je zweien teilerfremd annehmen; dann müssen wegen $x^2 + z^2 = 2y^2$ alle drei Zahlen x, y, z ungerade sein. Sei $2a$ der größte Teiler von $x - y$ und $y - z$; also

$$x - y = 2ac,\ y - z = 2ad,\ wo\ (c, d) = 1.$$

Dann ist $(x - y)(x + y) = (y - z)(y + z)$; also

$$c(x + y) = d(y + z).$$

Daher $y + z = \rho c,\ x + y = \rho d$.

Da c und d relativ prim, also nicht beide gerade sind, muß ρ gerade sein, $\rho = 2b$; also

$$x - y = 2ac,\ x + y = 2bd,\ y - z = 2ad,\ y + x = 2bc.$$

Hieraus folgt: $y = bd - ac$ und $y = ad + bc$. Durch Gleichsetzen kommt

$(b - a)d = (b + a)c$; also $\quad b + a = ad,\ b - a = ac$

$$2b = a(d + c),\ 2a = a(d - c).$$

Durch Einsetzen in die vorigen Equationen folgt:

$$\left.\begin{aligned} x - y &= ac(d - c),\\ x + y &= ad(d + c),\\ y - z &= ad(d - c),\\ y + z &= ac(d + c) \end{aligned}\right\} \text{ und daraus } x, y, z.$$

Damit x, y, z teilerfremd wird, muß $a = 1$ oder 2 sein.

Nun soll $x^2 - y^2 = v^2 > 0$ sein; also $a^2cd(d^2 - c^2) = v^2 > 0$.

Also $v = au$ und

$$\text{(A)} \qquad cd(d^2 - c^2) = u^2 > 0 \quad (c > 0, d > 0).$$

Ich beweise die Unmöglichkeit der Equation (A).

Bei der Solution von (A) kann man $(c, d) = 1$ voraussetzen; ferner darf man annehmen, dass c und d nicht beide ungerade sind; denn andernfalls setze man

$$d + c = 2d',\ d - c = 2c';$$

dann sind c', d' nicht beide ungerade, und (A) geht über in die analoge Equation $c'd'(d'^2 - c'^2) = \left(\frac{u}{2}\right)^2$.

Sei also jetzt

$$\text{(A)} \qquad cd(d^2 - c^2) = u^2 > 0,\ (c > 0, d > 0;\ (c, d) = 1;$$

c, d nicht beide ungerade).

Wegen $(c, d) = 1$ müssen c und d selbst Quadrate sein: $c^2 = c_1^2,\ d^2 = d_1^2$; also ist

$c_1^2 d_1^2 (d_1^4 - c_1^4) = u^2 > 0$, oder

$$\text{(B)} \qquad d_1^4 - c_1^4 = t^2 > 0.$$

Man erkennt daraus, da c_1 und d_1 nicht beide ungerade sind, daß d_1 ungerade, c_1 gerade ist.

Nach Solution der pythagoräischen Equation ist also

$$d_1^2 = m^2 + n^2, \quad c_1^2 = 2mn, \quad t = m^2 - n^2.$$

Hier müssen m und n teilerfremd sein ; dann folgt aus der ersten dieser Equationen wieder

$$\left.\begin{aligned} m &= r^2 - s^2 \\ n &= 2rs \end{aligned}\right\}$$ oder umgekehrt ; $(r, s) = 1$; r und s nicht beide ungerade. Dann ist aber $c_1^2 = 2mn = 4rs\ (r^2 - s^2)$; also c_1 gerade, und $rs\,(r^2 - s^2) = \left(\frac{c_1}{2}\right)^2 > 0$; $(r > 0, s > 0, (r, s) = 1$; r, s nicht beide ungerade).

Das ist nun wieder die Equation (A), wobei aber u durch die viel kleinere Number $\frac{c_1}{2}$ ersetzt ist $\left[\text{denn es ist } u^2 = c_1^2 d_1^2\ (d_1^4 - c_1^4) > c_1^2 d_1^2 > \left(\frac{c_1}{2}\right)^2\right]$. Also descente infinie.

IV. Ich gebe hier noch einige Eigentümlichkeiten des magischen Quadrats mit 3^2 Feldern an., welche noch unbekannt sind.

2 A	7 B	6 C
9 D	5 E	1 F
4 G	3 H	8 J

(1) Verbindet man A mit D und D mit F durch eine Linie, so entspricht die erhaltene Figur jener Figur, welche durch Verbindung von J mit H und H mit B entsteht und es ist $2^4 + 9^4 + 1^4 = 8^4 + 3^4 + 7^4$.

(2) Man bekommt alle Primzahlen von 17–43, wenn man je eine Eckzahl mit 5 multipliziert und je die nebenstehende Number zum Produkt addiert, also : $5 \cdot 2 + 7 = 17$; $5 \cdot 2 + 9 = 19$; $5 \cdot 4 + 3 = 23$; $5 \cdot 4 + 9 = 29$; $5 \cdot 6 + 1 = 31$; $5 \cdot 6 + 7 = 37$; $5 \cdot 8 + 1 = 41$; $5 \cdot 8 + 3 = 43$.

(3) Es bestehen noch diese regulären Relationen : $5 \cdot 7 + (2 \cdot 6) = 5 \cdot 3 + (4 \cdot 8)$ und $5 \cdot 9 + (2 \cdot 4) = 5 \cdot 1 + (6 \cdot 8)$.

REACTIVITY OF THE DOUBLE BOND IN COUMARINS AND RELATED α–β UNSATURATED CARBONYL COMPOUNDS.

Part IV. Action of Bromine on Coumaric Acids.

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Received September 14, 1937.

In connection with the elucidation of the constitution of certain mercury compounds derived from the coumarins,[1] the tribromo derivatives of coumarin and 7-methylcoumarin were required. There existed some difficulty in preparing them, since coumarin requires to be brominated in a sealed tube at about 150°[2] and since under the same conditions 7-methylcoumarin yields complex products. The action of bromine on coumaric acid was expected to solve this difficulty and as the preparation of the coumaric acids from the coumarins has been rendered simple by recent work in these laboratories, the method described in this paper should make the brominated coumarins readily available.

Simonis and Wenzel[3] treated coumaric acid with two molecular proportions of bromine in carbon disulphide solution and noticed that besides addition at the double bond, substitution in the ring in a position *para* to the hydroxyl group took place. The bromocoumaric acid dibromide thereby formed closed up the ring with the elimination of water and at the same time the unstable dibromide lost one molecule of hydrogen bromide to produce 3 : 6-dibromocoumarin.

In the experiments described in this paper, coumaric, 5-nitrocoumaric and 4-methylcoumaric acids have been treated with excess of bromine in boiling glacial acetic acid solution for 1 to 2 hours. The primary products of the reaction are found to be the dibromides of the coumarins with further bromine atoms, in the 6- and 8-positions if they are available for substitution. No free carboxylic acid is detected, complete conversion into the coumarins having taken place. This is obviously due to the addition of bromine at the double bond, thus facilitating the rotation of groups to enable ring closure.

The dibromides of the bromocoumarins undergo partial decomposition even during the preparation and the subsequent crystallisation and the brominated coumarins can be isolated pure by repeated crystallisations

alone. However, the readiest method is to treat the dibromides with cold alcoholic potash, when potassium bromide separates rapidly and the corresponding bromocoumarins are formed. Though the main products are 3 : 6 : 8-trisubstituted compounds, small quantities of partially brominated compounds are also isolated by working up the mother liquors. Thus coumaric acid yields 3 : 6 : 8-tribromocoumarin as the main product and 3 : 6-dibromo and 3-bromocoumarins as minor products. 5-nitrocoumaric acid gives as the main product 3 : 8-dibromo-6-nitrocoumarin and as byproduct 3-bromo-6-nitrocoumarin in a small yield. 4-methylcoumaric acid readily produces a good yield of 3 : 6 : 8-tribromo-7-methylcoumarin which is found to be the same as the one obtained from the mercury compound of 7-methylcoumarin.[1]

For purposes of comparison the action of bromine on 6-nitrocoumarin[4] has been reinvestigated and it has now been found that the initial product is 6-nitro-8-bromocoumarin dibromide which slowly decomposes during the process of heating and the subsequent repeated crystallisations to yield the required 3 : 8-dibromo-6-nitrocoumarin. Purification by repeated recrystallisations is rather tedious, since the decomposition of this dibromide is slow. With cold alcoholic potash, however, removal of the hydrogen bromide takes place very easily and hence the pure 3 : 8-dibromo derivative is obtained readily.

Experimental.

Action of bromine on coumaric acid. Preparation of 3 : 6 : 8-tribromocoumarin.—Coumaric acid (2 g.) was dissolved in boiling glacial acetic acid (15 c.c.) and a little over three molecular proportions of bromine (2·5 c.c.) dissolved in the same solvent (10 c.c.) was added. The mixture was boiled gently under reflux using a water condenser. There was a rapid absorption of bromine and a copious evolution of hydrogen bromide. The reaction was almost complete within an hour. The yield, however, increased by 0·5 g. on continuing the boiling for one hour more and further heating did not produce any improvement. When the solution was cooled at the end of the heating a pale brown solid separated out (3·5 g.). It was insoluble in aqueous sodium bicarbonate indicating that it was not an acid. It melted rather indefinitely between 180–93° C. After two crystallisations from glacial acetic acid using animal charcoal, it was obtained in the form of colourless thin needles melting at 199–200° C. (Found : Br, 63·0 ; $C_9H_3O_2Br_3$ required Br, 62·6%.) The melting point was unaffected when it was mixed with a sample of tribromocoumarin obtained by the method of Simonis and Wenzel.[2]

The crude product of bromination (2 g.) was suspended in ethyl alcohol (6 c.c.) and treated with alcoholic potash (1 g. in 4 c.c. of alcohol). The

suspension went into solution rapidly and potassium bromide separated out. After shaking for a few minutes the mixture was allowed to stand for about an hour with occasional agitation. It was then diluted with water and acidified. The colourless solid that separated out was rendered quite pure by one crystallisation from alcohol or acetic acid and was found to be identical with 3 : 6 : 8-tribromocoumarin. It was therefore, clear that the crude product contained considerable amount of dibromides which decomposed in cold alcoholic potash or in boiling acetic acid.

The mother liquor left after the separation of the above-mentioned pale-brown solid was diluted with water. This time a more deeply coloured solid was obtained. When this was treated with cold alcoholic potash as mentioned above potassium bromide separated out and the final product was a colourless solid from which by fractional crystallisation using alcohol small quantities of 3 : 6-dibromocoumarin melting at 183° C. and 3-bromocoumarin melting at 110° C. were isolated. If the treatment with alcoholic potash were omitted a rather prolonged series of crystallisations from alcohol using animal charcoal were necessary to obtain the compounds in a pure condition.

Treatment of coumaric acid with a large excess of bromine for about four hours did not appreciably increase the yield of the main product and in this case there was some complex decomposition and the lower bromination compounds could not be obtained.

On 5-nitrocoumaric acid. Preparation of 3 : 8-dibromo-6-nitrocoumarin.— In the methods described till now[5] for the preparation of 5-nitrocoumaric acid, red oxide of mercury was employed. It has now been found that by using the yellow oxide the yield is appreciably improved.

5-Nitrocoumaric acid (2 g.) was dissolved in sufficient quantity of boiling glacial acetic acid, a little over two molecular proportions of bromine added and the whole boiled for 2 hours. On cooling the solution, no solid separated out owing to the large volume of the solvent used. To the hot solution therefore water was added till it became cloudy and on cooling this time about 3 g. of a brown solid was formed. When subjected to the treatment with cold alcoholic potash as already described it gave a pale yellow solid, which after crystallisation from glacial acetic acid, melted at 218–19° C. and was found to be identical with 3 : 8-dibromo-6-nitrocoumarin obtained by the method of Dey and Row.[4] (Found : Br, 45·0 ; $C_9H_3O_4NBr_2$ required Br, 45·8 %.) The dibromo-nitrocoumarin could also be obtained from the crude product by repeated recrystallisations from glacial acetic acid using animal charcoal.

From the mother liquor after the isolation of the crude bromo-nitrocoumarin dibromide a somewhat resinous solid was obtained on adding water. On treatment with alcoholic potash it yielded a small amount of 3-bromo-6-nitrocoumarin melting at 215° C. after repeated crystallisations from acetic acid.

On 6-nitrocoumarin.—The procedure of Dey and Row[4] was adopted and the product was found to contain a considerable amount of the dibromide which decomposed during crystallisations comparatively slowly. A large number of recrystallisations from boiling glacial acetic acid (about 6) were therefore necessary to get a pure sample of 3 : 8-dibromo-6-nitrocoumarin melting at 218–19° C. This was, however, readily obtained from the crude material by the treatment with cold alcoholic potash for one hour and subsequent acidification after dilution with water. It crystallised from glacial acetic acid as prisms melting at 218–19° C. and was found to be identical with the specimen obtained from nitrocoumaric acid. By working up the mother liquor 3-bromo-6-nitrocoumarin melting at 215° C. was obtained in a small yield.

On 4-methylcoumaric acid. Preparation of 3 : 6 : 8-tribromo-7-methylcoumarin.—This acid (2 g.) in glacial acetic acid (15 c.c.) was treated with bromine (2·5 c.c.) in the same solvent (10 c.c.) and boiled for 2 hours. The crude product (yield 4 g.) readily gave 3 : 6 : 8-tribromo-7-methylcoumarin on treatment with cold alcoholic potash and this was found to be identical with the sample obtained from 7-methylcoumarin through mercuration and subsequent treatment with bromine.[1] It could not be obtained by the method of Simonis and Wenzel in which the methyl coumarin was treated in a sealed tube with bromine and water using a little iodine as a catalyst. Several experiments using temperatures between 120° and 150° C. yielded only indefinitely melting mixtures from which the tribromo derivative could not be isolated.

The pure tribromo-methylcoumarin which was easily obtained from the methylcoumaric acid crystallised from glacial acetic acid as colourless long narrow plates melting at 207–8° C. (Found : Br, 60·6 ; $C_{10}H_5O_2Br_3$ required Br, 60·4 %.) The coumarilic acid obtained by treatment with hot alcoholic potash crystallised from glacial acetic acid in the form of flat needles and melted at 270° C.

Summary.

By the action of bromine on coumaric, 4-methylcoumaric and 5-nitrocoumaric acids in boiling glacial acetic acid solution 3 : 6 : 8-tribromocoumarin, 3 : 6 : 8-tribromo-7-methylcoumarin and 3 : 8-dibromo-6-nitrocoumarin have been obtained in good yield. The primary products are the

dibromides of the bromo-compounds produced by the addition at the double bond, subsequent substitution in the nucleus and final ring closure. Hydrogen bromide gets slowly removed during the boiling and during the subsequent crystallisations so as to yield the above-mentioned bromo-coumarins. The best method for this however is to use cold alcoholic potash. Small quantities of the lower bromination products are also produced as by-products.

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ELLIPSOIDAL HARMONICS OF LARGE ORDERS.

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In a previous memoir,[1] the author obtained various expressions for Ellipsoidal Wave-functions. During the course of that work, it appeared that the methods adopted there would give useful results in the case of Ellipsoidal Harmonics also. Owing to other work, the publication of these results has been very much delayed.

In this paper asymptotic expressions for large orders of the functions and the characteristic constants are obtained.

The fundamental form of Lamé equation adopted in this paper is

$$d^2\mathrm{E}/d\xi^2 - \{n\,(n+1)\,k^2\,sn^2\,\xi + \mathrm{A}\}\,\mathrm{E} = 0 \qquad (1)$$

using Jacobian elliptic functions. n is an integer and A is one of the characteristic constants that will lead on solution to an Ellipsoidal Harmonic.

It has been shown by Whittaker[2] that the Ellipsoidal Harmonics satisfy elegant integral equations.

$$\mathrm{E}_n(\xi) = i\lambda \int_{\mathrm{K}-2i\mathrm{K}'}^{\mathrm{K}+2i\mathrm{K}'} \mathrm{P}_n\left(\frac{ik}{k'}\,cn\,\xi\,cn\,\eta\right)\mathrm{E}_n(\eta)\,d\eta \qquad (2)$$

$$\mathrm{E}_n(\xi) = \lambda \int_{-2\mathrm{K}}^{2\mathrm{K}} \mathrm{P}_n\left(\frac{1}{k'}\,dn\,\xi\,dn\,\eta\right)\mathrm{E}_n(\eta)\,d\eta \qquad (3)$$

$$\mathrm{E}_n(\xi) = \lambda \int_{-2\mathrm{K}}^{2\mathrm{K}} \mathrm{P}_n(k\,sn\,\xi\,sn\,\eta)\,\mathrm{E}_n(\eta)\,d\eta. \qquad (4)$$

The limits of integration for (2) have been changed to suit the conditions of the problem.

$$i\lambda \int_{\mathrm{K}-2i\mathrm{K}'}^{\mathrm{K}+2i\mathrm{K}'} \mathrm{P}_n\left(\frac{ik}{k'}\,cn\,\xi\,cn\,\eta\right)\mathrm{E}_n(\eta)\,d\eta$$

[1] See *The Ind. Jour. Phys.*, 1934, **9**, 45.

[2] *Proc. Lond. Math. Soc.*, 1915, **14**, (2), 260, and also Whittaker and Watson, *Modern Analysis*, 564.

can be written as

$$4i\lambda \int_{K}^{K+iK'} P_n\left(\frac{ik}{k'}\, cn\, \xi\, cn\, \eta\right) \psi\,(\eta)\, d\eta \qquad \text{where}$$

$$4\psi\,(\eta) = E_n\,(2iK' + 2K - \eta) + E_n\,(\eta) + (-)^n\, E_n\,(2K - \eta) + (-)^n\, E_n(\eta - 2iK')$$

$\psi\,(\eta)$ is a polynomial in $cn\,\eta$ and hence in the range of integration, it is continuous, bounded function with limited total fluctuation. According as

$$ik/k'\, cn\, \xi\, cn\, \eta \text{ is } > \text{or} < 1$$

$P_n\left(\frac{ik}{k'}\, cn\, \xi\, cn\, \eta\right)$ is asymptotically equivalent to

$$\frac{\exp\,(n + \tfrac{1}{2})\left\{\cosh^{-1}\frac{ik}{k'}\, cn\, \xi\, cn\, \eta\right\}}{\sqrt{2\pi n}\left\{-\frac{k^2}{k'^2}\, cn^2\, \xi\, cn^2\, \eta - 1\right\}^{\frac{1}{4}}}$$

or $$\sqrt{\frac{2}{n\pi}}\ \frac{\cos\left\{(n + \tfrac{1}{2})\ \arccos\frac{ik}{k'}\, cn\, \xi\, cn\, \eta - \pi/4\right\}}{\left(1 + \frac{k^2}{k'^2}\, cn^2\, \xi\, cn^2\, \eta\right)^{\frac{1}{4}}}$$

if n is large.

These forms show that the method of steepest descents could profitably be applied to obtain the dominant terms for the asymptotic expressions for $E_n\,(\xi)$. Writing the first expression as

$$\frac{\exp\,(n + \tfrac{1}{2})\cosh^{-1}\, cn\, \xi \cdot \exp -(n + \tfrac{1}{2})\left\{\cosh^{-1}\, cn\ \xi - \cosh^{-1}\frac{ik}{k'}\, cn\, \xi\, cn\, \eta\right\}}{\sqrt{2\pi n}\left\{-\frac{k^2}{k'^2}\, cn^2\, \xi\, cn^2\, \eta - 1\right\}^{\frac{1}{4}}}$$

it is seen that the main contribution to the integral is obtained in the neighbourhood of the point $\eta = K + iK'$. From the method of stationary phase, it is seen that if even the second form of $P_n\left(\frac{ik}{k'}\, cn\ \xi\ cn\, \eta\right)$ is used the main contribution is from the same point $\eta = K + iK'$. Hence it is sufficient to consider the asymptotic value for P_n when η is nearly $K + iK'$. In the present investigation it may be assumed that $cn\xi >> 1$. Then

$E_n\,(\xi) \sim$

$$\frac{4i\lambda}{\sqrt{2\pi n}} \cdot \exp\,(n + \tfrac{1}{2})\cosh^{-1}\, cn\, \xi \times \int_{K}^{K+iK'} \frac{\exp -(n + \tfrac{1}{2})\left\{\cosh^{-1}\, cn\ \xi - \cosh^{-1}\frac{ik}{k'}\, cn\, \xi\, cn\, \eta\right\}}{\left\{-\frac{k^2}{k'^2}\, cn^2\, \xi\, cn^2\, \eta - 1\right\}^{\frac{1}{4}}}\, \psi\,(\eta)\, d\eta. \quad (5)$$

To obtain the dominant term, it is sufficient if η is replaced by $\mathrm{K} + i\mathrm{K}'$ in the expression $\psi(\eta)\left\{-\frac{k^2}{k'^2}\, cn^2\,\xi\, cn^2\,\eta - 1\right\}^{-\frac{1}{4}}$ as it is bounded and has limited total fluctuation in the range of integration and the argument of the exponential term is expanded in terms of $\mathrm{K} + i\mathrm{K}' - \eta$ and terms higher than the square are neglected.

Putting $\eta = \mathrm{K} + i\mathrm{K}' - i\sigma$ it follows that

$$\mathrm{E}_n(\xi) \sim$$

$$-\frac{4\lambda}{\sqrt{2\pi n}}\{cn\,\xi + \sqrt{(cn^2\,\xi - 1)}\}^{n+\frac{1}{2}}\,\psi(\mathrm{K}+i\mathrm{K}')\,(cn^2\,\xi - 1)^{-\frac{1}{4}}$$

$$\times \int_0^{\mathrm{K}'} \exp\left(-\tfrac{1}{2}(n+\tfrac{1}{2})\,\frac{\sigma^2\, cn\,\xi}{\sqrt{(cn^2\,\xi - 1)}}\right) \cdot d\sigma$$

$$\sim -\frac{2\lambda\psi(\mathrm{K}+i\mathrm{K}')}{n\sqrt{cn\,\xi}}\{cn\,\xi + \sqrt{(cn^2\,\xi - 1)}\}^{n+\frac{1}{2}}. \tag{6}$$

As $\mathrm{E}_n(\xi)$ is a polynomial in $cn\,\xi$ it follows that

$$\mathrm{E}_n(\xi) \sim$$

$$-\frac{\lambda}{n}\{\mathrm{E}_n(\mathrm{K}+i\mathrm{K}') + (-)^n\,\mathrm{E}_n(\mathrm{K}-i\mathrm{K}')\}\,\frac{\{cn\,\xi + \sqrt{(cn^2\,\xi - 1)}\}^{n+\frac{1}{2}}}{\sqrt{cn\,\xi}}. \tag{7}$$

When the Ellipsoidal Harmonic is a polynomial in $dn\,\xi$ it follows from (3)

$$\mathrm{E}_n(\xi) \sim$$

$$\frac{\lambda}{nk}\{\mathrm{E}_n(0) + \mathrm{E}_n(2\mathrm{K})\}\left(\frac{dn\,\xi + kcn\,\xi}{k'}\right)^{n+\frac{1}{2}}\left(\frac{k'}{dn\,\xi}\right)^{\frac{1}{2}}. \tag{8}$$

Corresponding to (4)

$$\mathrm{E}_n(\xi) \sim$$

$$\frac{\lambda}{nk'}\{\mathrm{E}_n(\mathrm{K}) + (-)^n\,\mathrm{E}_n(-\mathrm{K})\}\,\frac{\{k\,sn\,\xi + \sqrt{(k^2\,sn^2\,\xi - 1)}\}^{n+\frac{1}{2}}}{\sqrt{k\,sn\,\xi}}. \tag{9}$$

The arguments $cn\,\xi + i\,sn\,\xi$; $dn\,\xi + k\,cn\,\xi$ and $k\,sn\,\xi + i\,dn\,\xi$ are doubly periodic functions of ξ. It follows that if equation (1) has asymptotic expansions of Horn and Jeffreys type in the form $\psi\,\epsilon^{(n+\frac{1}{2})\phi}$ the choice has to be limited by the condition that ϵ^{ϕ} is a doubly periodic function.

Let the following expansion be assumed :

$$\mathrm{E}_n(\xi) = \psi\,\epsilon^{(n+\frac{1}{2})\phi}\{1 + f_1/(n+\tfrac{1}{2}) + f_2/(n+\tfrac{1}{2})^2 + \cdots\}$$

$$\mathrm{A} = a_{-2}(n+\tfrac{1}{2})^2 + a_{-1}(n+\tfrac{1}{2}) + a_0 + a_1/(n+\tfrac{1}{2}) + \cdots$$

where $\psi, \phi, f_1, f_2 \cdots$ are functions of ξ only, $a_{-2}, a_{-1}, a_0 \cdots$ are constants and independent of n. Substituting the above in equation (1) and equating

coefficients of powers of $(n + \frac{1}{2})$ it is seen that

$$\phi'^2 - (k^2\, sn^2\, \xi + a_{-2}) = 0$$

$$\phi'' + \frac{2\phi'\psi'}{\psi} - a_{-1} = 0$$

$$2\phi' f_1' + \psi''/\psi - (a_0 - \tfrac{1}{4}\, k^2\, sn^2\, \xi) = 0$$

$$2\phi' f_2' + \psi'' f_1/\psi + 2\psi' f_1'/\psi + f_1'' - (a_0 - \tfrac{1}{4} k^2\, sn^2\ \xi)\, f_1 - a_1 = 0$$

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where dashes denote differentiation with respect to ξ ;

or

$$\psi = \frac{\text{const}\ \epsilon^{\pm \int a_{-1}\, d\xi / \sqrt{(a_{-2} + k^2\, sn^2\, \xi)}}}{(a_{-2} + k^2\, sn^2\, \xi)^{\frac{1}{4}}}$$

$$2f_1 + \frac{\psi'}{\psi\phi'} + \int \left\{ \frac{\psi'}{\psi} \left(\frac{\psi'}{\psi} + \frac{\phi''}{\phi'} \right) - a_0 + \frac{k^2}{4}\ sn^2\, \xi \right\} \frac{d\xi}{\phi'} = 0$$

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If ϵ^{ϕ} has to be a doubly-periodic function there are only three types of possible values for ϕ', namely, $\pm\, k\ sn\ \xi$; $\pm\, ik\ cn\ \xi$; $\pm\ i\ dn\ \xi$ corresponding to the following values of a_{-2} : 0, $-k^2$ and -1 respectively.

When $\phi' = \pm\ k\ sn\ \xi$ the value of ψ is

$$\frac{1}{\sqrt{sn\ \xi}} \left(\frac{dn\ \xi - cn\ \xi}{k'\ sn\ \xi} \right)^{\pm\, a_{-1}/2k}.$$

Hence to a first approximation

$$\mathrm{E}_n(\xi) = \frac{1}{\sqrt{\ sn\ \xi}} \left[\mathrm{A} \left(\frac{dn\ \xi - k\ cn\ \xi}{k'} \right)^{n\, +\, \frac{1}{2}} \left(\frac{dn\ \xi - cn\ \xi}{k'\ sn\ \xi} \right)^{a_{-1}/2k} + \mathrm{B} \left(\frac{dn\ \xi - k\ cn\ \xi}{k'} \right)^{-\, n\, -\, \frac{1}{2}} \left(\frac{dn\ \xi - cn\ \xi}{k'\ sn\ \xi} \right)^{-a_{-1}/2k} \right]$$

where A and B are constants. As $dn^2\xi - k^2 cn^2\xi = k'^2$ and $dn^2\xi - cn^2\xi = k'^2 sn^2\xi$ it follows that the function $\mathrm{E}_n(\xi)$ would be doubly-periodic and symmetrical about the usual points if and only if $\mathrm{A} = \pm\, \mathrm{B}$ and $a_{-1}/2k$ is $l + \frac{1}{2}$ where l is an integer. And

$$2f_1 - \left\{ \frac{-\,(2\,l + 1) \pm (l^2 + l + 1)\ cn\ \xi\ dn\ \xi}{2k\ sn^2\ \xi} \right\} \pm \frac{1}{k} \left\{ a_0 - \tfrac{1}{2}\,(1 + k^2)\,(l^2 + l + \tfrac{1}{2}) \right\} \log \frac{dn\ \xi - cn\ \xi}{k\ sn\ \xi} = 0$$

the constant of integration may be omitted as it will finally multiply the whole function by a constant. If f_{1+} and f_{1-} are the two values of f_1 corresponding to $\pm k\, sn\, \xi \pm \phi'$ then to a second approximation

$$E_n(\xi) = A\, \epsilon^{(n+\frac{1}{2})\phi}\, \psi_1 \left(1 + \frac{f_{1+}}{n+\frac{1}{2}}\right) + B\, \epsilon^{-(n+\frac{1}{2})\phi}\, \psi_2 \left(1 + \frac{f_{1-}}{n+\frac{1}{2}}\right).$$

But this function is not symmetrical or anti-symmetrical about $\xi = K$ with the condition $A = \pm B$ unless the logarithmic terms disappear. Hence

$$a_0 = \tfrac{1}{2}(1 + k^2)(l^2 + l + \tfrac{1}{2}).$$

Similarly at all stages of working it will be necessary to equate the coefficients of logarithmic terms to zero.

A statement of the values of the first three functions and the corresponding constants are given below :—

a_{-2}	ϕ'	$\epsilon^{(n+\frac{1}{2})\phi}$
0	$\pm k\, sn\, \xi$	$\left(\frac{dn\,\xi - k\, cn\, \xi}{k'}\right)^{\pm(n+\frac{1}{2})}$
$-k^2$	$\pm ik\, cn\, \xi$	$(dn\, \xi + ik\, sn\, \xi)^{\pm(n+\frac{1}{2})}$
-1	$\pm i\, dn\, \xi$	$(cn\, \xi + i\, sn\, \xi)^{\pm(n+\frac{1}{2})}$

a_{-1}	ψ
$2k(l+\frac{1}{2})$	$\frac{1}{\sqrt{sn\,\xi}}\left(\frac{dn\,\xi - cn\,\xi}{k'\, sn\, \xi}\right)^{\pm(l+\frac{1}{2})}$
$2ikk'(l+\frac{1}{2})$	$\frac{1}{\sqrt{cn\,\xi}}\left(\frac{dn\,\xi + k'\, sn\, \xi}{cn\, \xi}\right)^{\pm(l+\frac{1}{2})}$
$2k'(l+\frac{1}{2})$	$\frac{1}{\sqrt{dn\,\xi}}\left(\frac{cn\,\xi + ik'\, sn\, \xi}{dn\, \xi}\right)^{\pm(l+\frac{1}{2})}$

a_0	f_1
$\frac{1}{2}(1+k^2)\ (l^2+l+\frac{1}{2})$	$\dfrac{-(2l+1) \pm (l^2+l+1)\, cn\,\xi\, dn\,\xi}{4k\, sn^2\,\xi}$
$k'^2/_4 - l\,(l+1)\,(k^2-\frac{1}{2})$	$\dfrac{-(2l+1)\, k' \mp (l^2+l+1)\, sn\,\xi\, dn\,\xi}{4ik\, cn^2\,\xi}$
$\frac{1}{4}+\frac{1}{2}l\,(l+1)\,(1+k'^2)$	$\dfrac{-(2l+1)\, k' \pm l\,(l+1)\, k^2\, sn\,\xi\, cn\,\xi}{4i\, dn^2\,\xi}$

As usual, this last method of obtaining the asymptotic expansion is less cumbersome than the earlier adopted in this paper.

There are three distinct asymptotic expansions for the value of the characteristic constant as in the case of the Ellipsoidal Wave-functions. The first and the third lead to real values of A while the second expression gives a complex value of A. The exact significance of these complex values is not known.

The constants of the asymptotic expansions may easily be obtained by comparing them with the expressions obtained earlier by the method of steepest descents in (7), (8) and (9).

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